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Synthesis, characterization and degradability of polyamides derived from tartaric acid and diaminoethers

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Abstract

A series of novel polyamides derived from L or D-tartaric acid and α,ω-diaminoethers containing 1, 2, 3 or approximately 70 oxyethylene units in the main chain were synthesized and characterized. Polycondensation in solution of the diaminoethers with di-*O*-methyl tartaric acid activated as pentachlorophenyl ester was used for the synthesis of these poly(ether tartaramide)s. Polymerization degrees oscillated between 10 and 140 depending on the length of the oxyethylene segment. These polyamides are highly hygroscopic and soluble in water. They are semicrystalline with melting temperatures ranging from 50 to 190 °C, and thermally stable up to 250 °C. Chiro-optical properties were found to depend on the configuration of tartaric acid showing both high specific rotations and characteristic circular dichroism ellipticities. Definite X-ray diffraction patterns consistent with the crystalline nature of these polyamides were recorded. Racemates made of enantiomeric pairs were also examined and some evidence indicative of the existence of a crystalline structure different from that present in the optically pure components was found.

Keywords: Polyamide; Polytartaramide; Polyetheramide

1. Introduction

The use of carbohydrate derivatives to prepare polyamides is receiving increasing attention, not only due to the huge abundance of these raw materials but also to the promising properties that are being disclosed for these new type of polymers in recent investigations [1]. Specifically, carbohydrate containing polyamides seem to adopt unusual helical conformations [2], they show exceptionally high hydrophilicity, and they are biodegradable materials with potential applications in the biomedical field [3].

Tartaric acid is the aldaric acid most extensively used for the synthesis of linear polyamides based on carbohydrates. After the pioneer works of Minoura [4] and Ogata [5] in the 1960–1970, a sustained research on a wide variety of poly(tartaramide)s has been carried out [6]. Thus, stereorregular poly(tartaramide)s with the hydroxyl groups blocked as methylene ketal [7] or methyl ether [8], have been synthesized, and their structure and properties are thoroughly examined. Most of these polyamides are semicrystalline [9], thermally stable, and display acceptable mechanical behavior [10]. The effect of the enantiomeric composition of both stereocopolymers and racemic mixtures on the crystal structure has been also investigated [11].

It is well known that polyamides are not readily biodegradable polymers. Although it has been shown that poly(tartaramide)s hydrolyzed slowly under physiological conditions [12] and that they may be even degraded by certain microorganisms [13], their biodegradability is still insufficient for certain applications. Furthermore, the presence of carbohydrates moieties will enhance the biocompatibility of polyamides [14]. Nevertheless, one of the methods commonly used to improve the biomedical properties of a polymer is insertion of poly(ethylene oxide) segments. Thus, a number of biocompatible polymers containing poly(ethylene oxide) has been prepared and studied in this regards, and some of them, like segmented polyurethanes, have achieved commercial realization [15]. Specifically, some polyamides containing polyether segments have been described and shown to display good antithrombogenic properties [16].

In this paper we wish to report on a new class of

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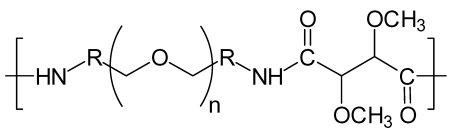
polyamides containing both carbohydrate units and ether groups. These poly(ether tartaramide)s are prepared from tartaric acid and α,ω-diaminoethers and they will be named PE*n*TA, where *n* indicates the number of ether linkages in the diamine counterpart (Fig. 1).

A study of poly(ether tartaramide)s bearing free hydroxyl groups, which are of interest for the design of controlled released systems, is the only reference found in the literature on these type of polyamides [17]. In this work we are dealing with poly(ether tartaramide)s, in which the hydroxyl groups of the tartaric unit have been protected as methyl ether in the way we used to do in previous work. Polyamides containing 1, 2, 3, and approximately 70 oxyethylene units in the main chain are synthesized and their crystalline structure, thermal properties and degradability are examined. Both enantiomerically pure poly-D and poly-L polyamides and their racemic mixtures have been included in this study in order to evaluate the influence of the enantiomeric composition on properties. Some years ago we reported extensively on poly(alkylene di-*O*-methyl D or L-tartaramide)s (P*n* DMDT or P*n* DMLT) obtained from di-*O*-methyl-D- or L-tartaric acid and alkanediamines [8]. Poly(ether tartaramide)s PE*n*TA can be regarded as coming from P*n* DMT by replacing one every three methylene units by oxygen. Comparison is made in this work between isometric PE*n*TA and P*n* DMT polyamides (polyamides having the same number of main chain atoms in the repeating unit) in order to appraise what is the influence of the presence of the oxy group on the structure and properties of poly(tartaramide)s (Fig. 1).

2. Experimental

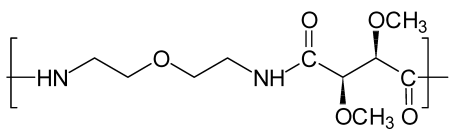
2.1. Materials and methods

All reagents and solvents were analytical grade or higher. They were used without further purification or, in the cases that needed, purified according to standard techniques. Viscosities were measured in dichloroacetic acid at 25.0 ± 0.1 °C by using an Ubbelohde microviscometer. Elemental analyses were carried out by Centro de Investigación y Desarrollo (CID-CSIC, Barcelona). Gel permeation chromatograms were acquired with a Waters instrument fitted with a 10^3 and 10^2 nm PL gel columns. Chloroform/*o*-chlorophenol (100:5, v/v) was used as eluent and calibration was made against polystyrene standards. IR spectra were recorded on a Perkin–Elmer 2000 spectrometer and NMR spectra on a Bruker AMX-300 spectrometer operating at 300.13 and 70.48 MHz for ^{1}H and ^{13}C, respectively. DSC thermograms were registered on a Perkin–Elmer DSC-4 instrument under a nitrogen atmosphere at 10 °C/min. Thermogravimetry analysis was carried out using a Mettler TA4000 thermobalance at a heating rate of 10 °C/min under inert atmosphere. Optical rotations were measured on a Perkin–Elmer 141 polarimeter

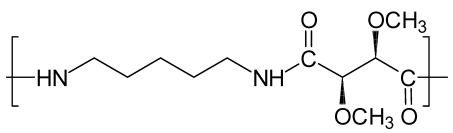


Polyetheramides PEnTA

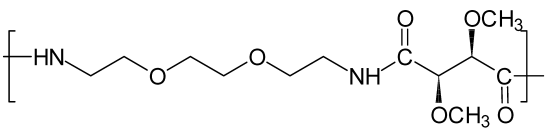
R = CH_2, n = 1: PE_1TA; n = 2: PE_2TA
R = CH_2CH_2, n = 3: PE_3TA
R = $OCONHCH_2CH_2$, n = 70: $PE_{70}TA$



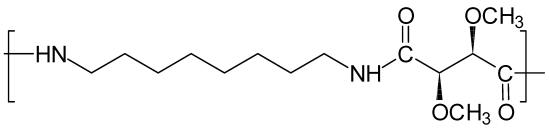
PE_1TA



P5DMLT



PE_2TA



P8DMLT

Fig. 1. General formula of poly(ether tartaramide)s PE*n*TA and isometric pairs PE*n*TA–P*n* DMLT polyamides.

at the sodium D line (589 nm) at 25 °C. Circular dichroism spectra were obtained at 25 °C, on a Jasco J-700 apparatus. Optical micrographs were recorded on a polarizing Nikon Labophot microscope. X-ray diffraction patterns were obtained in a Statton-type camera using nickel-filtered Cu Kα radiation of wavelength of 0.1542 nm and they were calibrated with molybdenum sulfide.

Diaminoethers (I-*n*) were purchased from Fluka, Merck or Sigma. It should be noted that some slight differences exist in the chemical structure of these diaminoethers. Whereas I-2 is similar to I-1 with an additional OCH_2CH_2, I-3 contains not only two additional OCH_2CH_2 units but also the amine end groups are attached to trimethylene units instead to ethylene units. On the other hand, I-70 has the amino end groups linked by an urethane group to the polyether chain and the number of OCH_2CH_2 units in the chain is not precisely defined. Since this compound is obtained from PEG with a number-average molecular weight of 3000, an average number of 70 OCH_2CH_2 units are estimated to be contained in I-70. The chemical formulae of these diaminoethers are shown in Fig. 1. Bis(pentachlorophenyl)-di-*O*-methyl-tartrates (II-L and II-D) were prepared according to previously described methods [8].

2.2. Synthesis of polymers

All manipulations were carried out under a nitrogen atmosphere with the solvents properly dried. A general procedure was used with small changes only affecting to the type of solvent used for the polycondensation reaction and to the working-up that is applied for recovering and purification of the polymer.

2.3. General procedure

Diamine I-*n* (4 mmol) was dissolved under stirring in the appropriate solvent (8 ml) at room temperature. Then the active diester II-L or II-D (4 mmol) was added in small portions and left to react for 3 days under stirring. Then the reaction mixture was heated at 60 °C for1–2 h. After cooling to room temperature, the formed polyamide was separated by precipitation and purified.

2.3.1. PE_1TA-L

Diaminoether I-1 in the dihydrochloride form was condensed with compound II-L in dimethyl sulfoxide and triethylamine was added to neutralize the released hydrochloride acid. The polymer was precipitated with a mixture of ether and isopropanol (1:1), washed thoroughly with this solvent, and dried under vacuum. Yield: 43%. Intrinsic viscosity: 0.41 dl/g. Elemental analyses calculated for $C_{10}H_{18}N_2O_5{\cdot}0.5H_2O$: C, 47.08; H: 7.50; N: 10.98. Found: C: 47.25; H: 7.56; N: 10.75. IR (cm^{-1}): 3305 (amide A), 3069 (amide B), 1660 (amide I), 1530 (amide II), 1129 (ethylene ether), 1095 (methyl ether). ^{1}H NMR ($CDCl_3$, ppm): 7.10 (t, N*H*, 2H), 4.25 (s, C*H*, 2H), 3.57 (m, CH_2–O, 4H), 3.53 (m, CH_2–NH, 4H), 3.42 (s, CH_3–O, 6H). ^{13}C NMR ($CDCl_3$, ppm): 169.8 (*C*O), 82.7 (*C*H), 69.3 (CH_2–O), 60.4 (CH_3–O), 38.3 (CH_2–NH).

2.3.2. PE_2TA-L and PE_2TA-D

Polycondensation of diaminoether II-2 with compound II-L or II-D was carried out in chloroform. The polyamide was precipitated with ether, repeatedly washed with this solvent, and finally dried under vacuum. Yield: 80%. Intrinsic viscosity: 1.16 and 0.86 dl/g for enantiomorphs L and D, respectively. Elemental analyses calculated for $C_{12}H_{22}N_2O_6{\cdot}1H_2O$: C, 46.74; H: 7.84; N: 9.08. Found: C: 46.73; H: 7.58; N: 9.01. IR (cm^{-1}): 3296 (amide A), 3067 (amide B), 1660 (amide I), 1531 (amide II), 1138 (ethylene ether), 1094 (methyl ether). ^{1}H NMR ($CDCl_3$, ppm): 7.10 (t, N*H*, 2H), 4.23 (s, C*H*, 2H), 3.61 (t, O–CH_2CH_2–O, 4H), 3.57 (m, CH_2–O, 4H), 3.54 (m, CH_2–NH, 4H), 3.43 (s, CH_3–O, 6H). ^{13}C NMR ($CDCl_3$, ppm): 169.7 (*C*O), 82.2 (*C*H), 70.3 (CH_2–O), 69.8 (O–CH_2CH_2–O), 60.5 (CH_3–O), 38.9 (CH_2–NH).

2.3.3. PE_3TA-L

Polycondensation of diaminoether I-3 with compound II-L was carried out in *N*-methyl pyrrolidone. The resulting polyamide was worked up in the same way as before. Yield: 82%. Intrinsic viscosity: 0.73 dl/g. Elemental analyses calculated for $C_{16}H_{30}N_2O_7{\cdot}0.5H_2O$: C, 51.75; H: 8.41; N: 7.54. Found: C: 51.36; H: 8.19; N: 7.50. IR (cm^{-1}): 3291 (amide A), 3066 (amide B), 1656 (amide I), 1532 (amide II), 1127 (ethylene ether), 1097 (methyl ether). ^{1}H NMR ($CDCl_3$, ppm): 7.02 (t, N*H*, 2H), 4.19 (s, C*H*, 2H), 3.6 (m, $(C_2H_4O)_2$, 8H), 3.55 (m, CH_2–O, 4H), 3.43 (m, CH_2–NH, 4H), 3.41 (s, CH_3–O, 6H), 1.85 (m, CH_2–CH_2–CH_2, 4H). ^{13}C NMR ($CDCl_3$, ppm): 169.5 (*C*O), 82.3 (*C*H), 70.6 and 70.4 ($(C_2H_4O)_2$), 69.3 (O–CH_2), 60.5 (CH_3–O), 37.0 (CH_2–NH), 29.5 (CH_2–CH_2–CH_2).

2.3.4. $PE_{70}TA$-L and $PE_{70}TA$-D

Polycondensation of diaminopolyether IV-70 with compound compound II-L or II-D was performed in chloroform and the resulting polyamides were processed as before. Yield, 78% and 86%, and intrinsic viscosity, 1.22 dl/g and 1.63 dl/g, for enantiomorphs L and D, respectively. Elemental analyses calculated for $C_{152}H_{300}N_4O_{77}$: C, 53.46; H: 9.55; N: 1.78. Found: C: 52.07; H: 8.92; N: 1.72. IR (cm^{-1}): 3340 (amide A), 1740 (urethane), 1664 (amide I), 1529 (amide II), 1148 (ethylene ether), 1111 (methyl ether). ^{1}H NMR ($CDCl_3$, ppm): 7.11 (t, NH amide, 2H), 5.40 (t, NH urethane, 2H) 4.15 (s, CH, 2H), 3.64 (m, $(C_2H_4O)_{70}$ and $(O–CO–NH–CH_2)_2$, ≈284H), 3.36 (m, CH_2–NH, 4H), 3.42 (s, CH_3–O, 6H). ^{13}C NMR ($CDCl_3$, ppm): 169.1 (CO), 156,8 (CO urethane), 82.5 (CH), 70. ($(C_2H_4O)_{68}$), 69.5 (O–CH_2–CH_2–O–CO–NH), 64,0 (O–CH_2–CH_2–O–CO–NH), 60.4 (CH_3–O), 40.7 (O–CO–NH–CH_2–CH_2–NH), 39.5 (O–CO–NH–CH_2–CH_2–NH).

3. Results and discussion

3.1. Synthesis of polymers

Polycondensations were performed according to Scheme 1. Some slight modifications have been introduced in the methodology previously used by us for the obtain a wide variety of poly(tartaramide)s [8]. Specifically, the diamine monomer was not converted in the *N*,*N*′-trimethylsilyl derivative since the diaminoethers were perfectly soluble in the polycondensation media and the reaction could proceed homogeneously with satisfactory yields. The relative low yield obtained for PE_1TA was due to the partial solubility of this polymer in the ether–isopropanol mixture that had to be used for the removal of the ammonium salts generated as by-products.

Elemental analysis results assessed the composition expected for PE*n*TA provided that some water is assumed to be present in the polymer. The presence of absorbed water not removable by usual methods has been reported to be common in poly(tartaramide)s and consistent with the hygroscopicity displayed by this type of polyamides [8,18]. IR spectra of PE*n*TA display the absorption bands characteristic of amide and ether groups. As shown in Fig. 2, the intensity of the characteristic oxyethylene band at about 1130 cm^{-1} relative to that of the methoxy band at 1095 cm^{-1} arising from the tartaric unit increased with the length of the polyether segment. Spectra of $PE_{70}TA$ show an additional strong band at 1720 cm^{-1} due to the urethane group. On the other hand the weak peak detected at 3420 cm^{-1} in PE*n*TA for $n = 1-3$ could be attributed to the non-associated amide groups present in the amorphous phase. This fact was confirmed by recording the IR spectra of PE*n*TA in dilute solution of $CHCl_3$; in these spectra, the band due to free NH was the only absorption observed in the amide A region.

Both ^1H and ^{13}C NMR spectra displayed signals whose chemical shifts and intensities were consistent with the

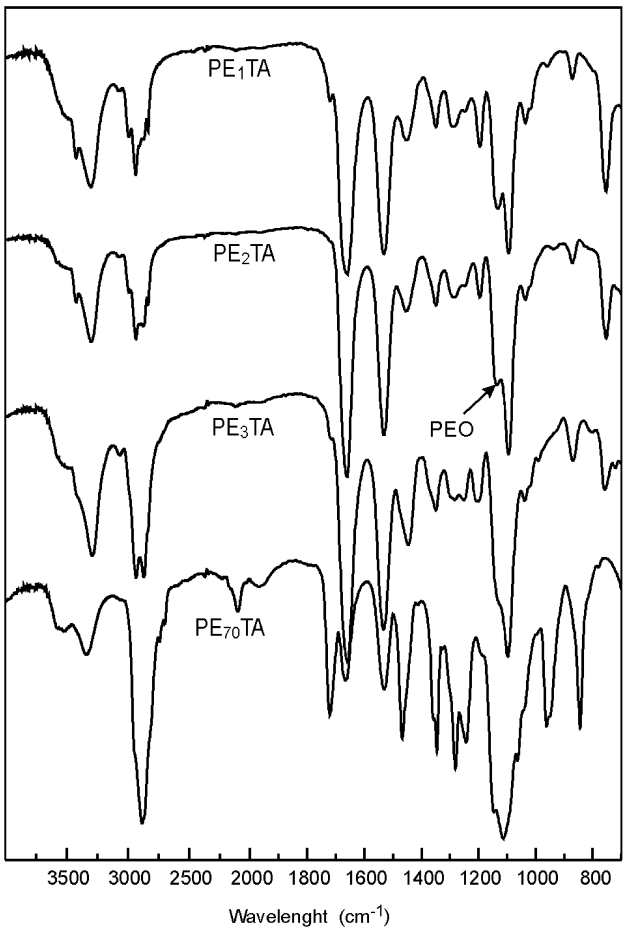
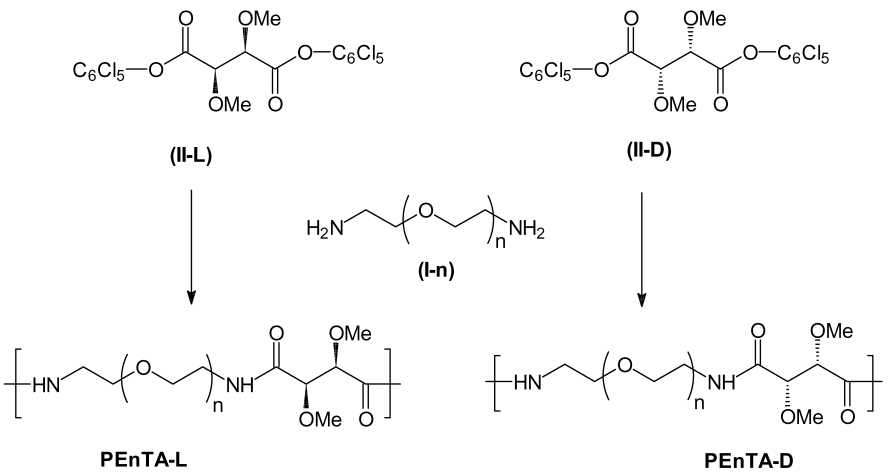


Fig. 2. IR spectra of PE*n*TA poly(ether tartaramide)s.

structure expected for these polymers. Oxyethylene protons appear between 3.35 and 3.5 ppm in ^1H NMR, while their carbons absorb near 39 and 70 ppm in ^{13}C NMR. Signals of tartaric unit appear as well resolved singlets in both ^1H NMR spectra, for the main chain methine protons, and ^{13}C NMR spectra, for the carbonyl groups. These data lead to conclude that racemization has not taken place in the



Scheme 1. Polycondensation reactions leading to poly(ether tartaramide)s PE*n*TA.

synthesis of these polyamides, at least at the level of sensitivity of the NMR technique. Poly(ether tartaramide) $PE_{70}TA$ spectra showed also the signals expected for the urethane groups present in these compounds Fig. 3.

Molecular weights of the poly(ether tartaramide)s were estimated by GPC and viscosimetry and the results are compared in Table 1. In general, intrinsic viscosity values are in accordance with molecular sizes determined by GPC, the discrepancies found in some cases probably due to differences in the flexibility of the polymer chain. Although molecular weights are satisfactory, the polymerization degree varies significantly from one polymer to other without reasonable explanation. Highest values were obtained for PE_2TA whereas almost oligomeric products resulted when polyetherdiamines were the compounds used as monomers.

Table 1
Molecular sizes of poly(ether tartaramide)s PE*n*TA

Polyamide	$[\eta]$ (dl g^{-1})	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$\bar{X}_n$
PE_1TA-L	0.41	23000	7300	3.15	30
PE_2TA-L	1.16	121000	41000	2.95	141
PE_2TA-D	0.86	92000	32000	2.87	110
PE_3TA-L	0.73	66000	14000	4.71	39
$PE_{70}TA$-L	1.22	64000	30000	2.13	12
$PE_{70}TA$-D	1.63	125000	63000	1.98	20

3.2. Solubility

The solubility behavior of these polyamides is shown in Table 2. It is seen that all these polyamides are soluble in water as well as in chlorinated solvents and formic acid. On

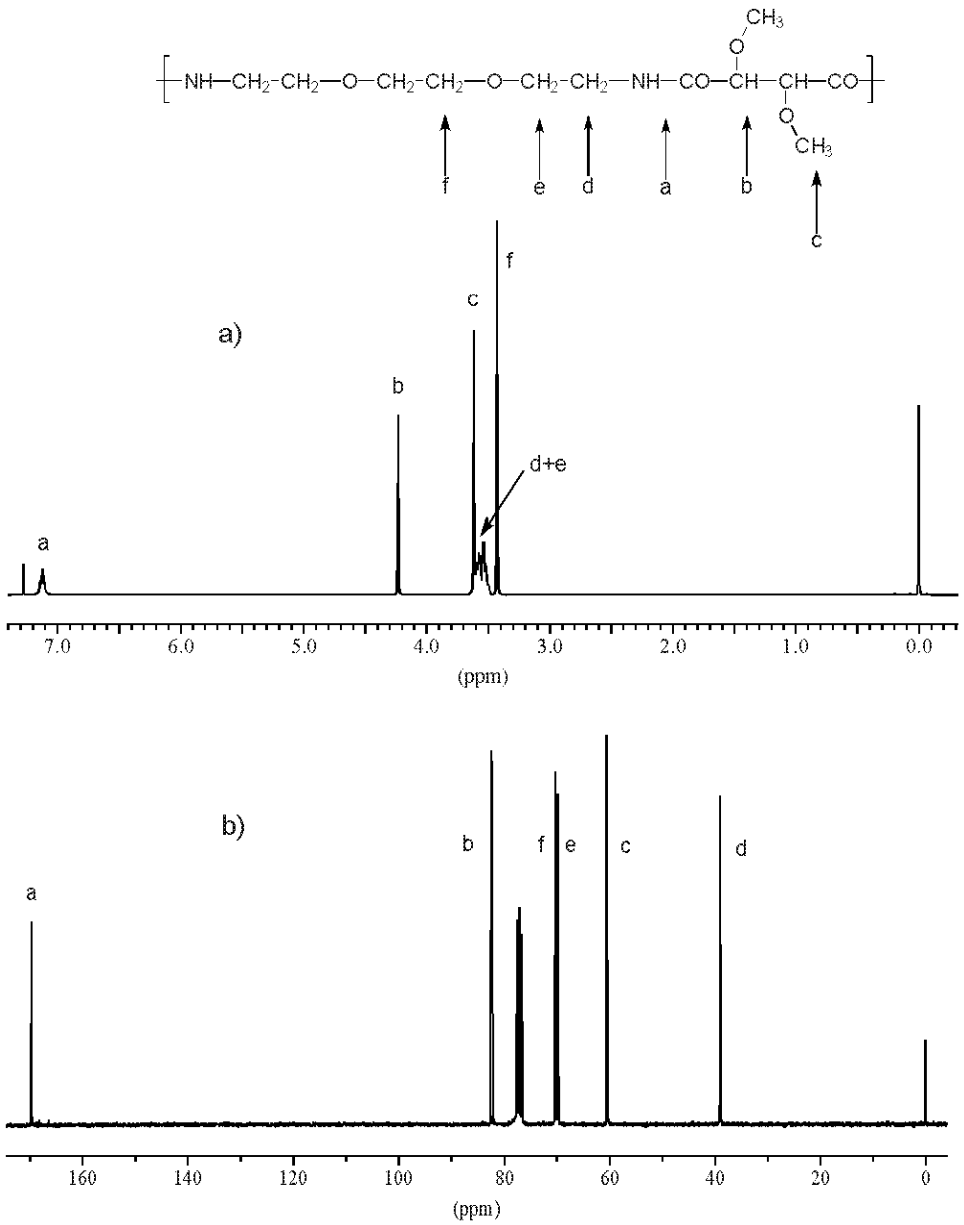


Fig. 3. NMR spectra of PE_2TA: (a) ^1H NMR spectrum, (b) ^{13}C NMR spectrum.

Table 2
Solubility of polyamides PE*n*TA

Solvent	PE_1TA	PE_2TA	PE_3TA	$PE_{70}TA$
Water	++	++	++	++
Acetone	−	+	+	++
Ethyl ether	−	−	−	−
Ethyl acetate	−	−	−	++
Ethanol	−	−	+	++
Chloroform	++	++	++	++
Dichlorometane	++	++	++	++
DMSO	±	++	++	±
DMF	±	+	+	++
Formic acid	++	++	++	++

Signs: ++ soluble; + soluble at 100 °C or at boiling point; ± partially soluble; − insoluble.

the contrary, they are not soluble in ether. PE_2TA and PE_3TA are partially soluble in acetone and the later is also partially soluble in ethanol. $PE_{70}TA$ is fully soluble in acetone, ethanol and ethyl acetate, This trend indicates the enhancing influence of the oxyethylene structure on the solubility of these polyamides to the point that the behavior of $PE_{70}TA$ in this regard is practically undistinguishable from that of poly(ethylene oxidel) (PEO).

Water absorption of PE*n*TA under 100% relative humidity was measured by weighting. The resulting curves representing water uptake against time are shown in Fig. 4. All of them behaved according to a common pattern, $PE_{70}TA$ being the most hygroscopic as expected from its higher content in oxyethylene units.

3.3. Chiro-optical properties

Due to the asymmetry of the tartaric unit, all these polyamides exhibit optical activity, which decreases steadily as the size of the constitutional repeating unit increases. As expected, enanthiomorphs pairs PE*n*TA-D and PE*n*TA-L show essentially the same absolute value but with opposite sign. Comparison of the optical activity of PE_1TA-L and PE_2TA-L with that showed by their corresponding isometric poly(tartaramide)s PDMLT-5 and PDMLT-8

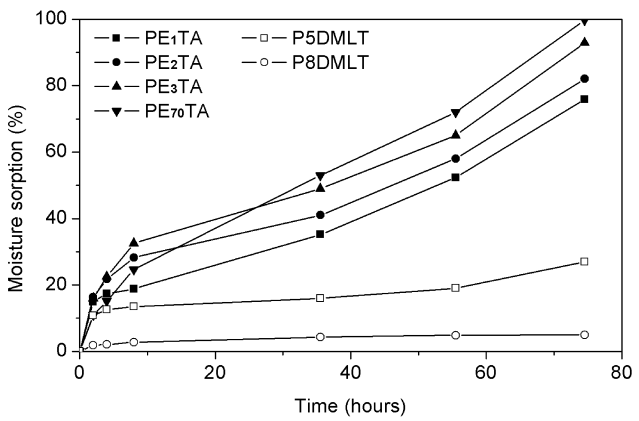


Fig. 4. Water uptake of PE*n*TA and P*n* DMLT with time.

revealed that both series behave similarly although specific optical rotations are lower for the present case. These data are compared in Table 3.

Circular dichroism spectra performed in either trifluoroethanol or water show a positive maximum at about 215 nm, which is shifted to 225 nm when the spectra were recorded in chloroform (Fig. 5). The traces are very similar to those observed for other chiral polyamides, for which the occurrence of regular secondary structure in solution has been claimed [19] This interpretation is supported by the fact that the 215–225 nm maximum disappeared when the spectra were recorded in methanesulphonic acid, which can be attributed to protonation of amide bonds and subsequent breaking of any possible regular conformation.

3.4. Thermal analysis

Thermogravimetric analysis showed that PE*n*TA with $n = 1–3$ start to decompose well above 200 °C and that decomposition occurs in two stages, the first one in the 250–350 °C range and the second one around to 400 °C. Representative decomposition curves are reproduced in Fig. 6 and decomposition temperature values for the two stages are listed in Table 3. The relative importance of the two decomposition steps varies steadily along the series, so that the second one increases in importance with the length of the polyether segment. The extreme situation was found for $PE_{70}TA$ where decomposition takes place almost exclusively at 400 °C. A plausible explanation could be that degradation of tartaric unit happens firstly, while decomposition of oxyethylene counterpart occurs at higher temperatures. It should be noticed that poly(ethylene oxide) (PEO) decomposes at about 350 °C, a temperature close to that observed for the second step of decomposition in PE*n*TA.

Thermal transitions associated to melting-crystallization processes were characterized by DSC. Samples coming straight from synthesis usually showed multiple endotherms which are explained as due to the fusion of different populations of crystallites with different sizes. After annealing definite single peaks were observed which were taken as the melting temperatures of these polyamides. On the other hand, traces recorded from quenched samples

Table 3
Optical and thermal properties of polyamides PE*n*TA

Polymer	$[\alpha]_D^{25}$ (°)	T_m (°C)	T_g (°C)	T_{d1} (°C)	T_{d2} (°C)
PE_1TA-L	+88.1 (0.96)	186	66	245	343
PE_2TA-L	+75.5 (1.04)	143	50	271	356
PE_2TA-D	−75.7 (0.99)	134	47	–	–
PE_3TA-L	+69.3 (0.99)	104	28	276	372
$PE_{70}TA$-L	+7.4 (0.95)	51	−49	250	372
$PE_{70}TA$-D	−6.0 (0.98)	49	−49	–	–
P5DMLT	+102.6 (0.50)	217	113	–	–
P8DMLT	+83.7 (0.51)	208	89	–	–

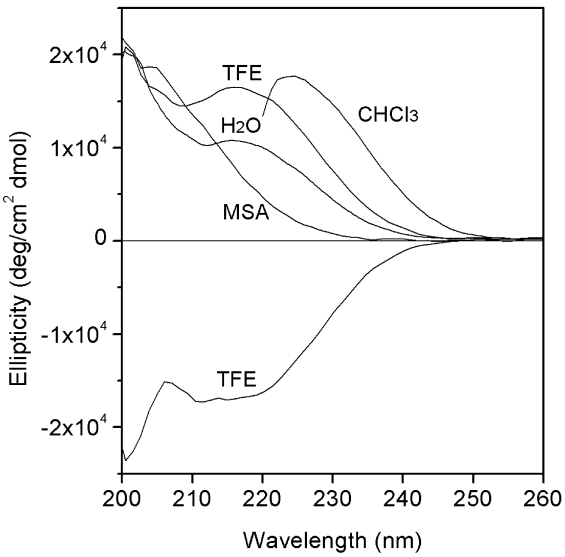


Fig. 5. CD signatures of PE_2TA in the indicated solvents. Positive and negative ellipticities were recorded for PE_2TA-L and PE_2TA-D, respectively.

displayed well-defined slope changes arising from second order transitions. DSC of PE_3TA are shown in Fig. 7 and melting and glass transitions temperatures for PE*n*TA are compiled in Table 3. As expected, T_m and T_g values are lower for PE*n*TA than for P*n* DMLT due to the higher chain flexibility of the formers afforded by the ether bond. Thermograms recorded at cooling showed no endotherm peak except for the $PE_{70}TA$. In this case, the highly flexible polyoxyethylene segment is able to move faster and crystallize. PE*n*TA films prepared by slow evaporation from chloroform solutions displayed well-defined spherulites confirming the crystalline nature of these polymers (Fig. 8(a)).

3.5. X-ray diffraction

X-ray diffraction patterns from the sample coming directly from synthesis consisted of well-defined ring reflections confirming the presence of remarkable crystal-

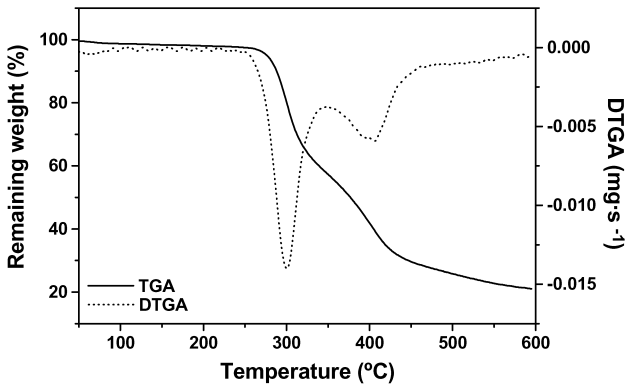


Fig. 6. TGA curve of PE_2TA and its derivative trace (heating rate: 10 °C/min).

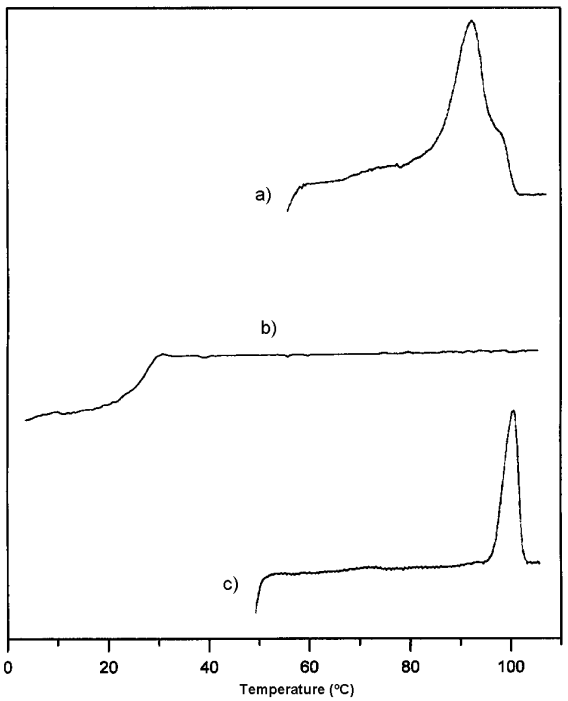


Fig. 7. DSC traces of PE_3TA (heating rate: 10 °C/min). (a) Sample directly from synthesis. (b) Second heating after rapid cooling in order to observe glass transition. (c) After annealing at 85 °C for 12 h.

linity in PE*n*TA (Fig. 8(b)). Bragg spacings measured for each polyamide are given in Table 4, where data for the poly(tartaramide)s P5DMLT and P8DMLT have been included for comparison. The highest spacing found in poly(ether tartaramide)s PE_1TA, PE_2TA and PE_3TA (10–16 Å) was found to increase with the length of the repeating unit and it could be associated to the axial repeat of the structure. Other intense reflections with spacing around 6 and 4.6 Å are comparable for the series as it could be expected for planes with index $l = 0$ of structures with the same pattern of side-by-side chain packing. Note that polyamides pairs PE_1TA/P5DMLT and PE_2TA/P8DMLT display essentially the same pattern indicating that the crystal structures adopted by the two isometric polyamides must be very similar. On the other hand, $PE_{70}TA$ produces a pattern almost undistinguishable from that obtained from POE confirming that the crystal properties of this polyamide is governed by the readily crystallizable polyether chain as it was discussed in the Section 3.4.

3.6. Analysis of PEnTA racemates

Racemic PE_2TA-R was prepared from PE_2TA-L and PE_2TA-D with similar molecular weights. Equimolecular amounts of the two optically pure polyamides were dissolved in chloroform and the solution left to evaporate slowly. Films thus prepared were studied by IR spectroscopy, DSC and X-ray diffraction. IR spectra and DSC thermograms did not show differences between the optically pure compounds and the racemate. However, X-ray

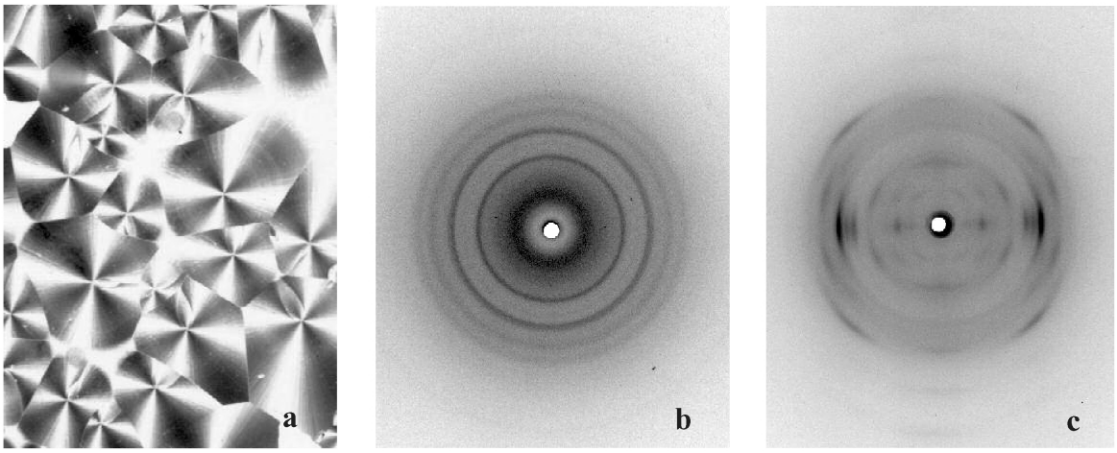


Fig. 8. (a) Spherulites of PE_2TA-L grown by slow evaporation of a chloroform solution (× 30). (b) Powder X-ray diffraction pattern of PE_2TA-L. (c) Fiber X-ray diffraction pattern of PE_2TA-R (fiber axis vertical).

diffraction revealed certain deviations in both spacing and intensities of reflections, which suggested that a different crystal structure from the enantiomeric pure PE_2TA could be present. At difference with the optically pure products, the racemate could be uniaxially stretched. More than fifteen independent reflections were detected in the fiber X-ray diffraction pattern obtained from an oriented sample of PE*n*TA-R, the which is reproduced in Fig. 8(c). All these spacings could be indexed on the basis of an orthogonal unit cell with parameters $a = 4.90$ Å, $b = 20.91$ Å, and $c = 14.67$ Å (Table 4). The density calculated for this structure containing two enantiomeric chains in the unit cell is 1.28 g ml^{-1} which is in full agreement with the value experimentally measured by the flotation method in CCl_4/ether.

3.7. Degradation in aqueous media

To evaluate the influence of the oxyethylene on the susceptibility of poly(tartaramide)s to hydrolysis, a sample of polyamide PE_2TA was incubated in water under physiological conditions (phosphate buffer pH 7.4, 37 °C) and the degradation process was followed by viscometry. The variation of intrinsic viscosity with time is plotted in Fig. 9. Data for the isometric polyamide P8DMLT are also plotted for comparison. It is clearly shown that the insertion

Table 4
Bragg spacings of polyamides PE*n*TA and their isometric P*n*DMLT poly(tartaramide)s

PE_1TA-L	P5DMLT	PE_2TA-L	P8DMLT	PE_3TA-L	PE_2TA-R[a] Obs	Calc (hkl)[b]
10.3 w	10.5 vs	13.0 w	12.70 s	15.80 m	10.30 s	10.46 (0 2 0)
6.42 vw	6.20 s	6.10 s	6.18 s	6.45 vw	5.23 s	5.23 (0 4 0)
5.80 s	5.85 vs			5.83 s	4.88 m	4.90 (1 0 0)
		5.23 w	5.18 w	5.51 m	4.42 vs	4.44 (1 2 0)
4.89 w	4.88 s	4.61 s	4.60 s	4.98 m	2.45 m	2.45 (2 0 0)
4.53 s	4.52 vs			4.55 s		
4.26 w	4.26 m			4.24 m	12.07 w	12.01 (0 1 1)
3.75 m	3.83 m	3.89 w	3.93 s	4.01 w	8.56 w	8.51 (0 2 1)
3.36 w	3.48 s	3.46 w	3.53 m	3.74 s	6.34 m	6.30 (0 3 1)
3.06 vw	3.07 w	3.13 vw	3.12 w	3.16 w	4.30 w	4.25 (1 2 1)
2.88 w	2.87 w				3.91 m	3.87 (1 3 1)
2.52 w	2.50 w	2.51 w	2.50 m		~7.15 w	7.35 (0 0 2)
					6.95 m	6.92 (0 1 2)
					4.04 w	4.08 (1 0 2)
					3.47 s	3.46 (1 0 3)
					3.66 vw	3.67 (0 0 4)
					2.90 vw	2.90 (0 1 5)
					2.48 vw	2.50 (1 1 5)
					2.44 vw	2.44 (0 0 6)

Intensities: vs: very strong; s: strong; m: medium; w: weak; vw: very weak.
[a] Data afforded by the fiber diffraction pattern.
[b] Calculated and indexed for the orthogonal unit cell: $a = 4.90$ Å, $b = 20.91$ Å, and $c = 14.67$ Å.

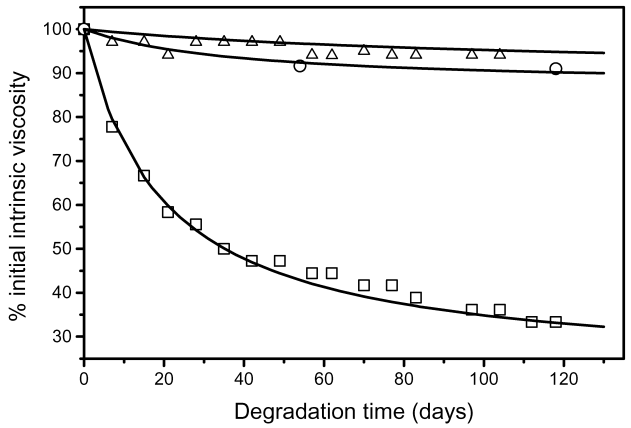


Fig. 9. Hydrolytic degradation behaviour of polyetheramide PE_2TA at pH = 7.4 (squares) and in saline solution (NaCl 0.9%) (triangles). For comparison degradation of P8DMLT at pH = 7.4 is included (circles), data from Ref. [12].

of the ether group in the polytartaramide chain enhances drastically the hydrodegradability of the polyamide to water. Obviously, the main reason that should be invoked for such behavior is that PE_2TA becomes solubilized in the degradation medium whereas degradation of non-soluble P8DMLThas to proceed under heterogeneous conditions. Although it is difficult to appraise, the influence of the oxy group on the reactivity of the amide bond toward hydrolysis should not be neglected. According to the general rule, the withdrawing character of this group is expected to enhance the nucleophilicity of the amide carbon making it more susceptible to the attack by water. Fig. 9 also shows the result of the treatment of PE_2TA with 0.9% NaCl solution. Surprisingly the typical exponential decay was not observed but viscosity practically remained constant with time. Although there is not fully convincing explanation for this observation, shielding of the polymer by salt solvatation of the ether group could be a plausible reason. It can be also argued that a closer conformation caused by saline effect would hide the amide groups hindering the attack by water.

3.8. Concluding remarks

The polycondensation method widely used before to obtain poly(alkylene tartaramide)s has been has proven to be valid also for the synthesis of poly(ether tartaramide)s. In this case however amine activation was not required since diaminoethers are soluble in the reaction solvent. Poly(ether tartaramide)s are water soluble polymers and thermally stable up to 250 °C. In the solid state they crystallized displaying melting points between 50 and 90 °C. Optically compensated seem to adopt a different crystalline structure from that present in the pure enantiomorphs suggesting the formation of stereocomplexes. These (polyether amide)s undergo hydrolysis much faster than their isometric poly(alkylene tartaramide)s, so that they became extensively degrade in water under physiological conditions in a couple of months.

Acknowledgements

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